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QUADRUPOLE MASS SPECTROMETER FOR
DIRECT SAMPLING OF ATMOSPHERIC GASES
AND CONDENSATION PRODUCTS

Sin-Shong Lin

Army Materials and Mechanics Research Center
Watertown, Massachusetts

March 1973

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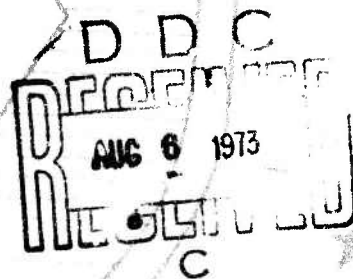
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SIN-SHONG LIN
MATERIALS SCIENCES DIVISION



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Technical Report by
SIN-SHONG LIN

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ABSTRACT

An apparatus for sampling atmospheric gases and condensation products has been designed and fabricated. A quadrupole mass spectrometer and modulated beam technique were used for beam detection. The design detail and the system performance are described and results are briefly presented. The sensitivity of the sampling device reaches parts per million, and numerous large clusters and aggregates generated from supercooling of gases during sampling processes were detected.

CONTENTS

	Page
ABSTRACT	
INTRODUCTION	1
DESIGN	1
EXPERIMENTAL	6
RESULTS	9
DISCUSSION AND SUMMARY	13
ACKNOWLEDGMENT	14

INTRODUCTION

The quadrupole mass spectrometer has proven to be an extremely versatile mass analyzer in studying numerous problems in various scientific disciplines. The compact size as well as the light weight makes this instrument very attractive in many fields, especially in airborne investigation. Although there are a few shortcomings associated with the mass filter, the present improved performance and economic considerations have substantially enlarged the field of application. One of the inherent disadvantages of the mass filter is that the transmission of ions in the quadrupole field depends on their masses, and the mass resolution of the instrument has to be compensated with the ion transmittances. This situation has hindered further usages of the mass filter to detect heavy ions encountered in sampling large organic molecules, bio-molecules and clusters. Various attempts^{1,2} have been proposed to overcome this difficulty, however they are not practical for immediate uses.

Although direct line-of-sight analyses of gas compositions by other mass spectrometers have been known for years, the application of the quadrupole mass filter in this field for detection of high molecular weight clusters is seldom seen. The unique feature of the arrangement is to analyze the composition of vapor phase without losing vapor constituents from collisions, surface reactions, and precipitation of sampling probes. Thus, reactive species, radicals, condensates and clusters in atmosphere, transpiration cell, flame, combustion, rocket exhaust and vapor deposition process could be conveniently detected. This report describes the design and technical aspects of using the quadrupole mass filter and beam modulation for detection of large polymers and clusters generated from jet expansion of atmosphere pressure gases, and experimental results of several gases are briefly presented.

DESIGN

1. General Description

To introduce atmospheric pressure gases into the quadrupole mass spectrometer for analysis, the pressure of the gas to be sampled must be reduced to 10^{-4} atm or better. However, it is preferable to have high vacuum for this purpose in order that a high density flux jet can be formed and the spectrometer will operate at the maximum efficiency. The stringent pumping requirement to produce a high intensity jet has been described by Kantrowitz and

¹MARMAT, P., The Journal of Vacuum Science and Technology, 8, 262 (1971)

²DAWSON, P. H., International Journal of Mass Spectrometry and Ion Physics, 6, 33 (1971)

Grey³, and Anderson, Andres, and Fenn⁴ in detail and will not be described here. In short, the pumping speed required to produce a jet beam should be fast enough to remove the volume of the incoming gas from a small orifice, i.e., the minimum pumping rate is the ratio of the pressure of the gas source to that of the expansion chamber multiplied by the volume of the incoming gas. Other factors such as scattering of gas, residual, desorbed gases, surface areas, and surface properties of the vacuum chamber will increase the required speed by a factor of two or more. In the present design, the dimension of the chambers as well as the conductance of gas flow were kept as large as possible under practical limits to reduce the resistance of flow. The distances between the chambers to the pump exits were kept short and minimum numbers of elbows were used to construct the vacuum system. The sketch of the vacuum system as well as the essential parts of the sampling device are shown in Figure 1. Three-stage differential pumping is used to maintain high vacuum in the detector region, and the vacuum pumps used in each stage are listed in Table I.

Table I. PUMPING ARRANGEMENT IN THE SAMPLING SYSTEM

Chamber	Function	Pumping Speed (Liter/sec)		Pressure ^c
		Diffusion ^a Pump	Forepump ^b	
1st	Jet beam formation	1400	1500	2×10^{-4}
2nd	Beam modulation	680	500	2×10^{-5}
3rd	Beam detection	680	150	less than 1×10^{-6}

- (a) All oil diffusion pumps are made by T-H Vacuum Products, Riverton, N.J. Sizes are 1400 liter/sec for six-inch and 680 liter/sec for four-inch pumps.
- (b) Forepumps are obtained from the Welch Scientific Company, Skokie, Illinois. Models 1378, 1398, and 1402B have capacities of 1500, 500 and 150 liter/sec respectively.
- (c) Pressure readings are recorded from one atmospheric air and a 0.0085-cm-dia. jet orifice. Vacuum gages are located at the flanged necks of each chamber.

³KANTROWITZ, A., and GREY, J., The Review of Scientific Instruments, 22, 328 (1951)

⁴ANDERSON, J. B., ANDRES, R. P., and FENN, J. B., Advance in Chemical Physics, vol. X, (editor John Ross, Interscience Publishers, New York, 1966) pp 275

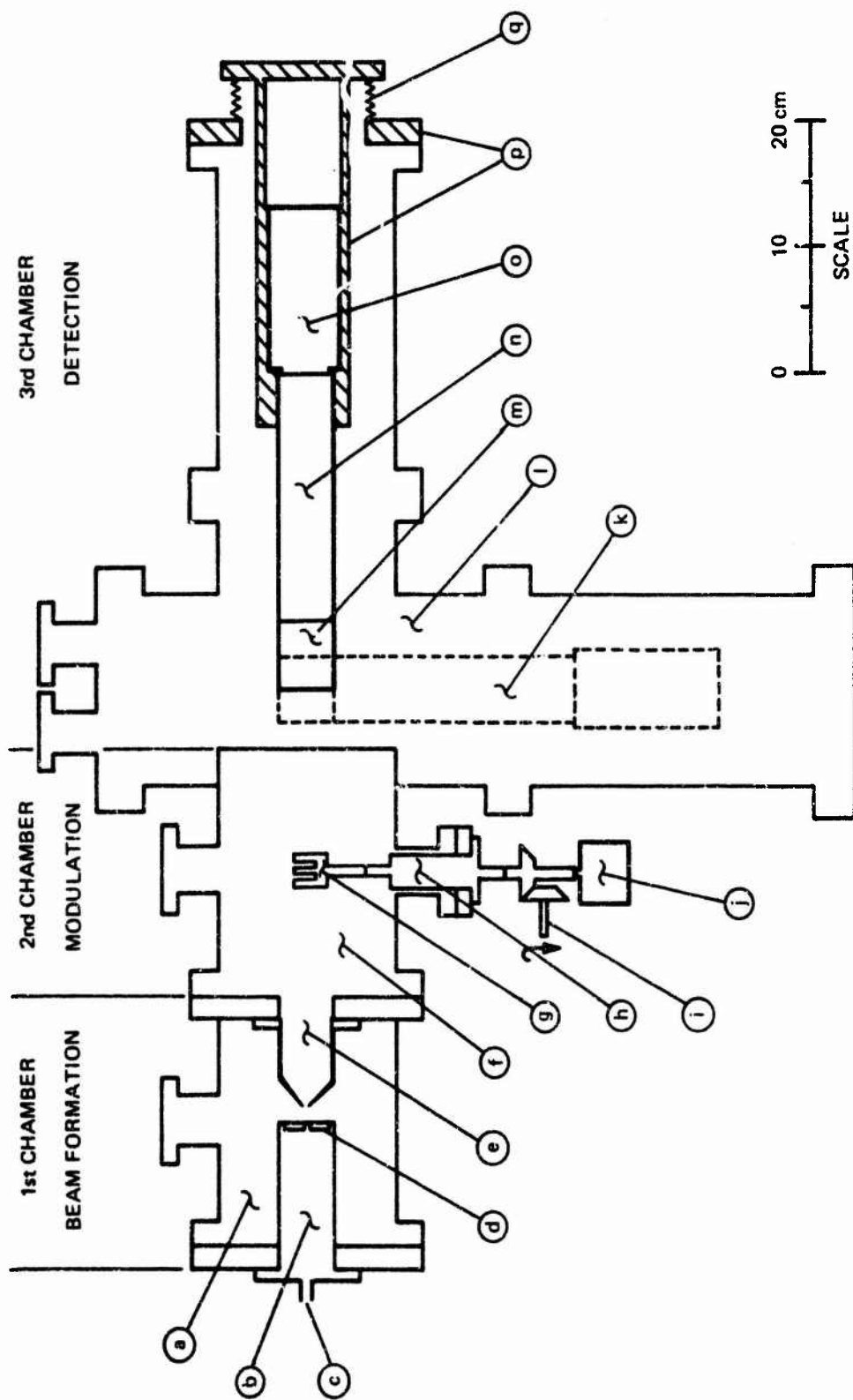


Figure 1. Schematic Diagram of Sampling Device

Figure 1 Schematic Diagram of Sampling Device

- (a) 1st Chamber, beam formation
- (b) cylindrical gas source
- (c) gas inlet from reservoir
- (d) orifice flange
- (e) skimmer
- (f) 2nd chamber, beam modulation
- (g) chopping wheel
- (h) magnetic type feedthrough
- (i) right angle gear
- (j) photoelectric rotary switch
- (k) additional space for a detector
- (l) 3rd chamber, beam detection
- (m) ionizer of mass filter
- (n) quadrupoles of mass filter
- (o) electron multiplier of mass filter
- (p) spectrometer mounting flange and support
- (q) bellow, part of the mounting flange

The present sampling system consists of three sections isolated from each other by small orifices. Each section is evacuated by a pumping assembly including a liquid nitrogen trap, an oil diffusion pump, and a large size mechanical pump. All structures in high vacuum regions are constructed from standard size stainless steel tubes and bakable flanges of a copper gasket type. As illustrated in Figure 1, the first section of the system is the expansion chamber in which a jet beam is produced. This chamber contains a gas source and a skimmer. The second chamber serves as a buffer zone for reducing pressure and also provides a large space for housing the modulation mechanism. The third chamber accommodates a quadrupole mass spectrometer for beam detection and also furnishes additional space for a second detector. The jet beam passage is determined by two small orifices located on the partition walls of the three chambers. Two or three small flanged necks are attached to each chamber to provide installation ports for vacuum gages, view windows, and feedthroughs. The system was designed for easy assembly and accessibility.

2. First chamber, beam formation

The main function of this chamber is to reduce the atmospheric pressure of the sampling gas to form a supersonic high intensity jet. The six-inch pump, provided with a fairly large and fast pumping speed, was used to maintain the lowest possible pressure in this expansion chamber. As indicated in Figure 1, most of the chamber space is occupied by a cylindrical gas source and a cone-shaped skimmer. One end of the gas source cylinder provides an O-ring groove on which a jet orifice flange is fastened, and the other end is pressed against the Viton gasket on the high vacuum flange of the chamber. The latter arrangement is made to insure that the jet orifice can be maneuvered and aligned for the passage of the jet beam.

The dimension of the sampling orifice is chosen from the standpoint that the orifice is large enough to produce a high flux jet from atmospheric gases without degrading the vacuum of the chamber. Poor vacuum in the expansion chamber will result in a low jet intensity due to scattering and collisions. Since a six-inch pump was used, the maximum diameter of the orifice was kept under 0.0085 cm. Two types of orifice were made: one is a channel roughly 0.025 cm thick, and the other a thin orifice. The orifice of the former was made by laser drilling a 0.25-cm stainless steel plate and of the latter by arc sparking a 0.00125-cm-thick nickel foil. The channel orifice gives a higher resistance to gas flow than the thin orifice, consequently, the vacuum gage reading in the expansion chamber for the channel orifice is better than the thin one of the same dimension.

The skimmer design is adopted from the recommendation of J. B. Anderson, R.P. Andres, and J.B. Fenn⁵. An orifice opening of 2 mm diameter was made on the tip of the cone, and the base of the cone was welded to a short cylinder.

⁵ANDERSON, J. B., ANDRES, R. P., and FENN, J. B., Advance in Atomic and Molecular Physics, vol. 1, (editor D. R. Bates and Immanuel Estermann, Academic Press, New York, 1965) pp 345

The skimmer was flanged on to the partition wall to the second chamber. The distance between the skimmer orifice and the jet orifice of the gas source affects the characteristics of the jet being sampled. The skimmer was placed 1.27 cm from the jet orifice, which was far enough downstream from the jet expansion mask and was in the region of free molecular flow.

3. Second chamber, beam modulation

This chamber is used as a buffer zone for pressure transition, and also contains a chopping mechanism to modulate the jet beam. A platform was placed in this chamber to support extra mechanisms such as velocity selector, magnetic and electric deflectors. The chamber is four liters in volume and is evacuated by a four-inch diffusion pump backed by a large forepump. The chopping wheel is made from a 2.54-cm-diameter rod with six slit openings, which are cut parallel to the axis of the rod and are equally spaced on the cylindrical surface. The chopper rod is rotated perpendicular to the beam path so that the jet flux is intersected by the motion of these slits. The modulation wheel is externally driven by a motor through a magnetic fluid type feedthrough mounted on the flanged neck attached to the chamber. The motion of the chopper is duplicated by a photoelectric type rotary switch coupled directly to the axis of the rotation. Thus a reference signal is generated by the switch which differs only by a phase angle from the actual position of the chopper wheel.

4. Third chamber, beam detection

This chamber is designed to accommodate the mass spectrometer under moderately high vacuum. The pole assembly under vacuum consists of ionizer, quadrupoles, and multiplier, occupying a volume which is 7 cm diameter x 45 cm long. Thus, the chamber is constructed large enough to house and to manipulate the pole assembly, and also provides an additional space for a second mass filter. This chamber and the second one are linked only by a 2-mm-diameter slot. The straight line formed by this slot and the skimmer orifice should be in sight with the entrance aperture of the ionizer for perfect alignment. For this purpose, a special flange for mounting and positioning the mass spectrometer was fabricated. The design detail of the mounting flange has been described in a previous publication⁶.

EXPERIMENTAL

1. Materials.

The gas reagents for this experiment to test the present sampling device were obtained from the Matheson Co., Inc. All gases are research grade of at

⁶SIN-SHONG LIN, The Review of Scientific Instruments, 42, 1083 (1971)

least 99.9% purity. They were used without further purification. The vapor-saturated gases were prepared by bubbling gases successively through three washing bottles containing water or methanol.

2. Quadrupole mass spectrometer

The quadrupole mass spectrometer used for the detection of the jet beam is manufactured by Extranuclear Laboratories, Inc., Pittsburgh, Pennsylvania. The pole is Model No. 162-8 which has a rod of 0.953 cm diameter and 20.32 cm long. The quadrupole assembly under vacuum consists of a high efficiency ionizer, poles, and a 14-stage Cu-Be electron multiplier. The assembly is arranged in such a way that the axes of the ionizer and poles are coincident with the molecular beam and the axis of the multiplier is paraxial to the beam.

The type II high efficiency electron impact ionizer has an 0.318-cm entrance hole aperture and a maximum ionization electron current of 50 ma. The ion optics of the ionizer consists of two planar and two cylindrical lenses for collimation. The apertures of these lenses are larger than the first entrance aperture of neutral beam, consequently, each neutral particle has only a single pass through the ionizer rather than striking surfaces and scattering back to the ionization region.

The rf and dc fields in the poles are supplied by the power system Model QPS-D₂. At the maximum peak rf voltage of 3.2 kV, dc voltage of 470 V, and at 1.6 Mc, the highest mass number, 950 amu, can be reached. The mass resolution can be varied through either constant $m/\Delta m$ and/or constant Δm modes. In addition, a dc bias potential is provided for operation off ground voltage. This dc voltage is used to trim the observed mass peak to a desirable shape. The best resolution obtainable is 350 at 350 amu based on the 10% peak-to-peak definition.

The detector consists of a 14-stage π type Be-Cu electron multiplier, a tuned preamplifier electrometer, a lock-in amplifier, an oscilloscope, and an x-y recorder for signal display. The high potential supplied to the electron multiplier can be set at 3 kV which gives a multiplier gain in the order of 10^5 . The output from the multiplier goes through a 10^7 ohm series resistance to provide a signal for the preamplifier and the lock-in amplifier. The lock-in amplifier is operated at a fixed reference frequency of 80 Hz generated from the rotary switch which is coupled to the chopping wheel.

3. Procedure

The experimental procedure for detection of the jet beam is as follows: The quadrupole mass spectrometer is operated in the sweep mode so that a wide range of the background ion spectrum can be shown on the oscilloscope screen as described in the manual provided for this instrument. The spectrum on the screen is carefully examined for any pickup signals while the chopping mechanism is activated and the lock-in amplifier is tuned to the reference

frequency. The gas to be sampled is introduced, and the ion signals resulting from the gas will enhance their intensities shown on the spectrum. However, if the spectrometer is not completely out of alignment with the beam path, the ion signals of the gas should be modulated in accordance with the rotation of the chopping wheel. The sweep mode of the display is then switched to the manual control mode so that the magnitude of an ion signal from the sampling gas can be recorded on the output meter of the lock-in amplifier. All instrumental controls are then adjusted to maximize the peak intensity shown on the panel meter at a fixed resolution setting and a suitable ion source condition.

Next, the entrance hole of the mass filter and the jet orifice of the gas source are to be aligned with the beam passage determined by the skimmer orifice and the second slot. The former is accomplished by adjusting x and y motion knobs of the specially designed mounting flange of the mass filter so the first aperture of the ionizer can be centered on the beam path. Then the jet orifice is placed into the beam path by sliding the entire gas source on the O-ring gasket mounted on the flange of the first chamber. The optimum adjustments in both cases are made by observing the positions at which maximum deflections of the ion signal occur.

After the signal from the sampling gas has been obtained and has been optimized with respect to the instrumental controls, a slow scan is made to examine the peak shapes of the transmitted ions. The fine resolution Δm , and pole bias controls may be used to trim the ion peaks and/or increase the intensities to a desired magnitude. A compromise is made between the peak intensity and the resolution. For the best detection of high mass ions, the resolution is lowered to compensate for the transmittance of the ions. The largest mass number observed in this instrument is mass 924 amu, from $(\text{CO}_2)_{21}^+$ ion at a resolution of 150, that is, the profile of the ion recorded on the spectrum is spread over a mass range of 7 amu.

The transmissions of the high mass ions in the quadrupole field are found to be negligibly small when the instrument is operated at a high resolution. The ion intensity at a given mass number increases drastically with decreasing resolution until a plateau value is reached. Thus, an adequate resolution in which the instrument provided a good sensitivity for the ions must be searched. A reasonable sensitivity of the high mass ion is obtained by lowering the resolution to the extent that the ion intensity will not increase considerably. Other controls, such as Δm and pole bias, are also adjusted in a similar manner to optimize the peak width. The procedure described above is repeated from one mass peak to the next higher mass peak until a satisfactory result is obtained.

Since the peak width as well as the shape changes considerably with the mass number, the intensity measured by taking the maximum reading at a fixed mass number is misleading. This phenomenon is especially pronounced at low resolution where a large distortion of the quadrupole field occurs. Often an ion peak is found to consist of several maxima spread over a wide mass range. Thus, the measurement of ion signal by integrating peak area is preferable.

RESULTS

1. Beam density

The gas expanded through a small orifice into vacuum forms a well-collimated high density jet beam. Several gas samples are used to examine the intensities of the jet beam. The observed relative ion signals of the gases are shown in Table II. The ion detector is operated at the same condition for all gases being sampled. The first and the second columns show the ion signals of interest; the modulated signals obtained from the lock-in amplifier at a reference frequency of 80 Hz are shown in the third column, and the experimental parameters are briefly described in the last column. Only the ion intensity of helium is calibrated and is shown in the fourth column. This calibration was performed by comparing the ion signal obtained from a standard leak and the apparatus geometry. Since the pumping rates of the expansion chamber are different for different gases being sampled, no direct comparison could be made from their relative ion intensities.

The theoretical expression of the intensity of jet beam has been given by Packer et al⁷, and will not be repeated here. Under ideal expansion and minimum scattering, the calculated density of the jet attainable from one-atmosphere source pressure is on the order of 10^{16} particles/cm²/sec. The present sampling device produces a jet flux of helium, 2×10^{15} atom/cm²/sec as indicated in column 4, Table II, which is about one order of magnitude lower than the value predicted. Since the helium has a high diffusibility and also a moderate vacuum is found in the first chamber, the beam flux might have been partially scattered and reduced.

The sensitivity of the device can achieve one part of 180,000 under average background noises. The isotope of argon in laboratory air was readily measurable by increasing the multiplier voltage to 3 kV and by setting the electron ionization current to 10 ma. The modulated signal of the isotope $^{38}\text{Ar}^+$ recorded on the lock-in amplifier is 0.1 mv under signal-to-noise ratio of 5 to 1 and a time constant of 300 msec.

2. Detection of cluster ions

During the course of sampling atmospheric gases through a small orifice, the adiabatic expansion causes supercooling of the gas so that enormous supersaturation will dominate the process. As a result, an extensive condensation and nucleation will take place during the beam formation. The extent of supersaturation is determined by expansion ratio, specific heat ratio of gas, and the initial source condition. Complications may arise during the expansion history because energy states of the molecules are not presently known.

⁷PARKER, H. M., KUHLETHAU, A. R., ZAPUTA, R. N., and SCOTT, JR., J. E., Rarefied Gas Dynamics (Pergamon Press, Inc., New York, 1960) pp 69

Table II. ION SIGNALS OF SEVERAL GASES EXPANDED FROM ONE ATMOSPHERE PRESSURE SOURCES

Gas	Mass (amu)	Ion Signal (mv)	Beam Density (atom/cm ² , sec)	Remarks
H ₂	2	46	-----	The instrument is set at 1-kV multiplier voltage, 4-ma. ionization current, and a thin orifice of 0.0085-cm size.
He	4	20	2.06 x 10 ¹⁵	
N ₂	28	30	-----	
Ar	40	42	-----	
CO ₂	44	24	-----	

The gas sources of H₂, He, N₂, Ar, and CO₂, and water- and methanol-saturated gases of H₂, He, N₂, and Ar have been used in testing the present device. When H₂, He, and N₂ gases from one atmospheric pressure sources were expanded through a thin orifice of 0.0085 cm dia., only small concentrations of dimer ions were observed. However, large numbers of polymer ions Ar_n⁺, n up to 10, were found at a source pressure of 3 atm. These results are identical to those reported by Milne and Greene⁸ under similar source conditions. The large numbers of cluster ions were observed in the sampling process of CO₂, especially at higher pressures. The relative intensities of the CO₂ cluster ions obtained from three source pressures are shown in Figure 2. The abscissa of the figure indicates mass number in atomic mass unit, and also in units of the monomer mass. A detectable signal of the cluster ion (CO₂)₂₁⁺ is observed which is almost at the limit of the mass scale of the detector.

The water - and methanol-saturated gases from one-atmosphere sources give predominantly the ions of which a proton is attached to neutral polymers, such as H(H₂O)_n⁺ and H(CH₃OH)_n⁺. Because of a relatively low vapor water pressure in the carrier gases at room temperature, the largest water cluster ion observed in argon carrier gas was H(H₂O)₁₂⁺. But for methanol-saturated gases, the large cluster ions up to n = 27 polymer, were detected. Figure 3 shows results obtained for methanol vapors in three carrier gases. The atomic compositions for large methanol polymers were uncertain because the resolution of the instrument was only at 150.

⁸MILNE, THOMAS A., and GREENE, FRANK T., The Journal of Chemical Physics, 47, 4095 (1967)

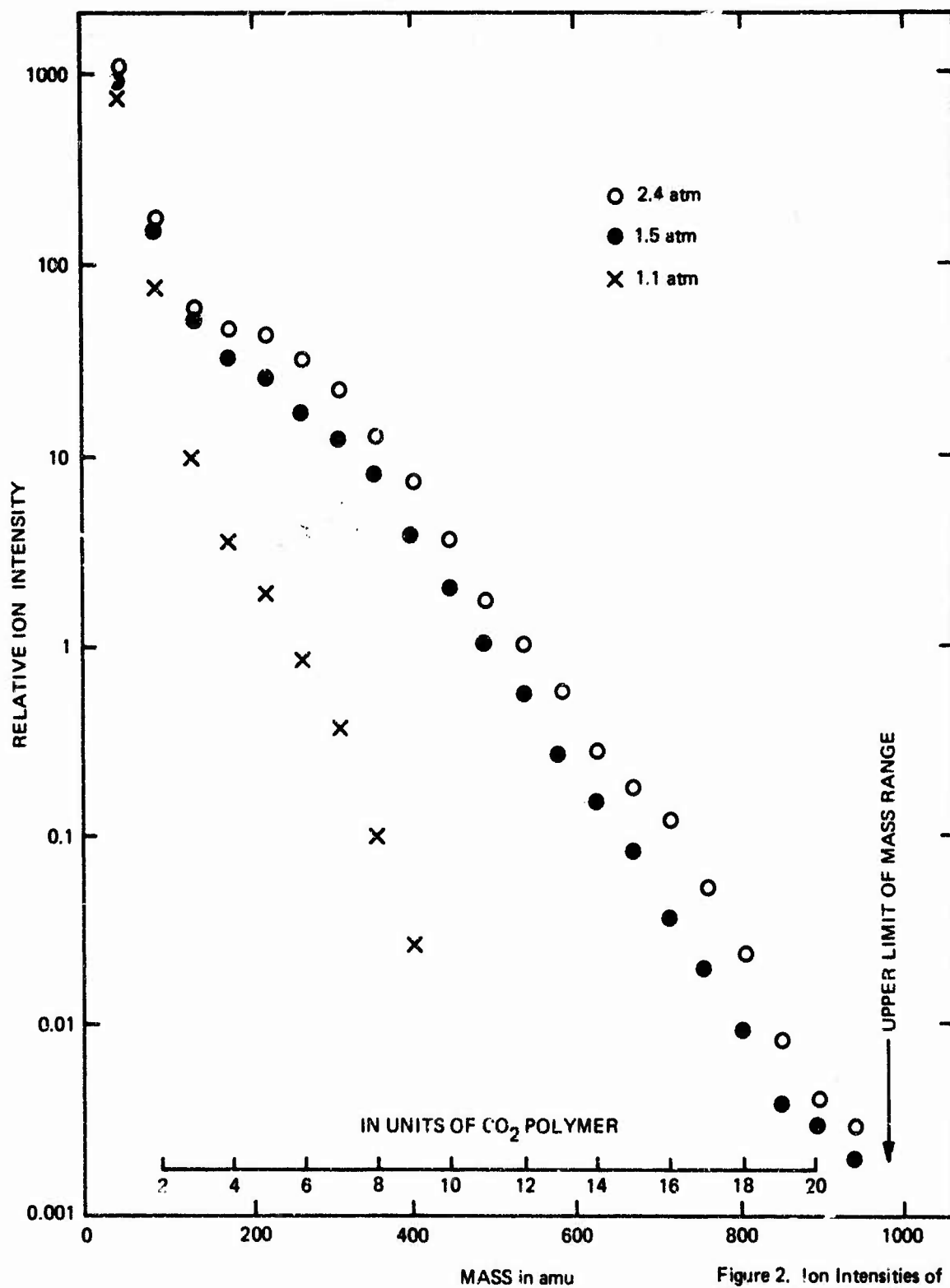


Figure 2. Ion Intensities of Carbon Dioxide Clusters From a Jet Orifice of 0.0085 cm Dia.

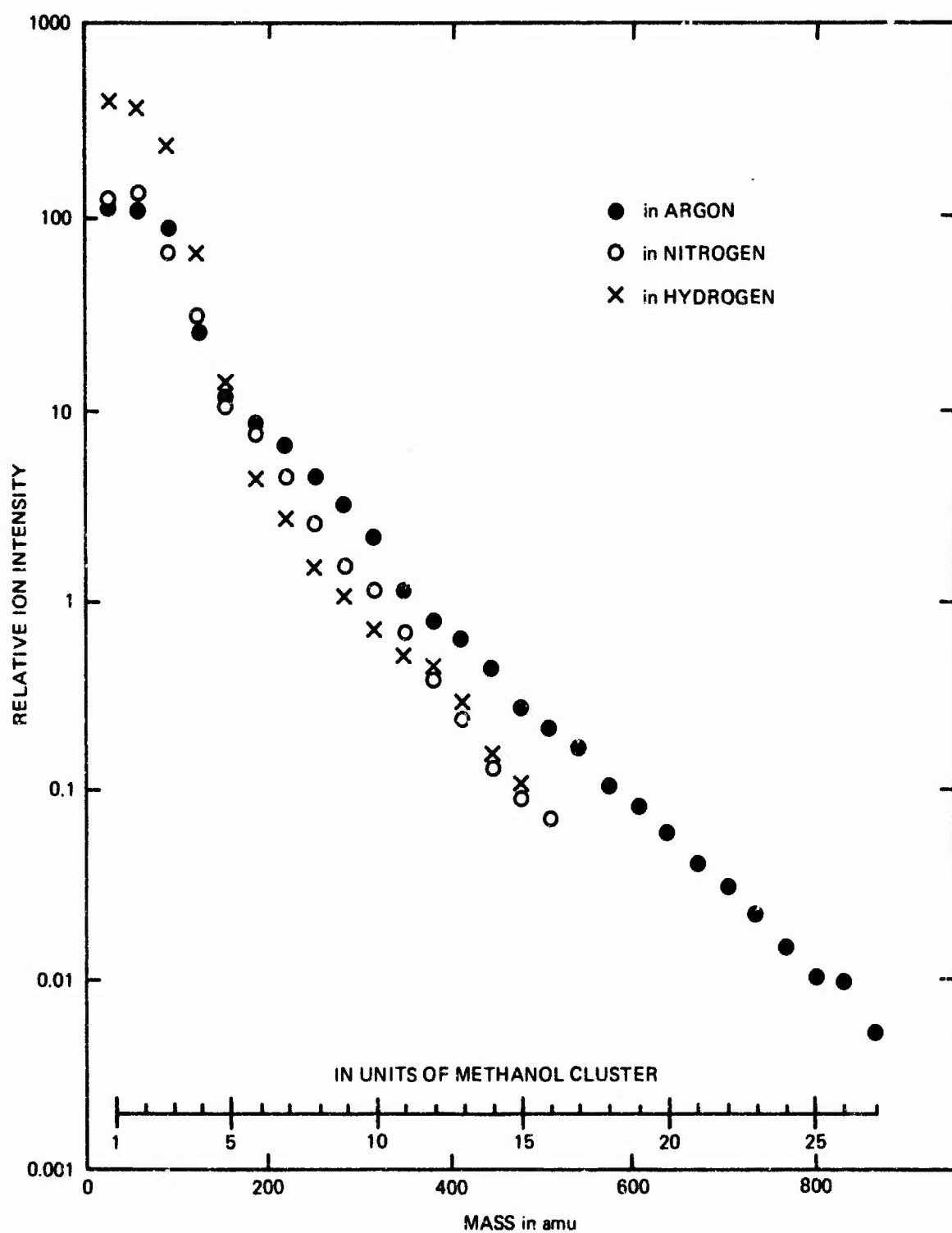


Figure 3. Ion Intensities of Methanol Clusters From Carrier Gas at One Atmosphere Pressure

DISCUSSION AND SUMMARY

The device to sample atmospheric pressure gases through a small orifice has been fabricated and the performance has been evaluated. The observed jet flux density generated from one atmosphere helium source is in the order of 10^{15} atom/cm² sec. This density is less than the one predicted by theory. The rather simple design and the limited pumping capacity of the present system have demonstrated that a reasonably good intensity of the jet beam can be produced. Since the pumping of the expansion chamber is provided only from a six-inch pump with a moderate speed of 1400 liter/sec, the jet intensity could be improved by increasing the pumping capacity and/or cryogenic cooling of the expansion chamber and the skimmer. Thus the jet density could be improved by an order of magnitude.

In the present design, the flow of the jet is restricted by the cross-section of the entrance hole of the detection chamber. The dimensions of the skimmer and the entrance hole are both 2 mm in diameter. The size of the skimmer orifice seems to be unnecessarily large. This will certainly degrade the vacuum and will produce additional scattering in the modulation chamber. From the apparatus geometry, the diameter of the skimmer orifice could be reduced to one third of the present dimension without affecting the jet intensity.

The beam modulation technique coupled with a conventional quadrupole mass spectrometer is a useful tool to detect large clusters up to the mass limit of the detector. The condensation products from supersaturation of gases during the adiabatic expansion process are readily observable by this arrangement. Although the mass resolution of the detector has to be lowered to compensate for the sensitivity to heavy ions, the detected signals are clearly distinguished from background noises and are originated from the jet beam. Some difficulties might be encountered in using this technique for the detection of large mass ions separated by a few mass units, such as organic polymers and biomolecules. However, in these cases, if the intensities of the large ions are comparatively high, the resolution of the mass filter could be set at a higher value to identify their masses. For non-hydrogen-containing compounds, such as carbon dioxide clusters as shown in Figure 2, no such difficulty was found.

In short, the present design gives a moderate jet beam intensity suitable to be used in a wide variety of research, such as high density beam experiments, atmospheric sampling, pollution control, nucleation studies, and polymer research. This system demonstrates that jet flux of a moderate intensity is produced from a comparatively simple and economic design, and the quadrupole mass filter coupled with beam modulation technique can be used to detect large mass ions.

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